Evolution and Regulatory Impact of Fumed Inorganic Materials in Toners

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Abstract

This presentation will describe how two nano-structured inorganic material classes which are produced by flame processes have been crucial to the technical evolution of the toner industry during the past two decades: fumed metal oxides as external additives and carbon black as the essential pigment. Market forces driving this evolution and increasing additive diversity are the demand for high speed office printers and commercial digital presses and the need for low priced laser printers to make small office and home (SOHO) use affordable. Additionally, eco-friendly printers with reduced energy consumption and zero emissions require the development of toner with low fusing temperatures (low T_g*) based on environmentally safe raw materials. Novel fumed silicon/titanium mixed oxides offer the positive tribo-charging benefits of titanium dioxide combined with the surface properties of silica. Acting as effective spacers that prevent re-agglomeration of low* T_g *toner, fumed sub-micron particles based on both silica and titania have distinct advantages over precipitated and sol-gel-derived materials, respectively. These include; low moisture, high purity, and the complete absence of internal porosity. For improved dispersibility and optimized toner surface coverage, de-agglomerated, chemical and mechanical structure-modified fumed metal oxides have been developed and will be discussed. Lastly, the paper will explore the impact of the ongoing EH&S (environmental, health & safety) discussion on external additives, carbon black and development trends toward safe external additives.*

1. Introduction

The non-impact printing revolution could be said to have begun with the invention of electro-photography in 1938. Today, together with ink jet printing, electro-photography is making inroads into all traditional areas of commercial printing like offset printing due to its high degree of flexibility.

The break-through of bringing individualized printing into the home and office was initiated by ink jet printing technology in the 1980s; the mainstay of electro-photography in its early days was as the office copier. These technologies have led to the creation of a large market in on-demand printing and copying.

Without the development of the external fumed silica additives 30 years ago, toner technology would not have become as successful and widespread as it has; bringing with it professional quality printing into convenient, everyday use.

High resolution images created by ink jet printing have also been greatly impacted by the application of fumed metal oxides as the ink receiving layer for ink jet paper. The unique particle morphology and surface chemistry of fumed metal oxides increases the paper ink receptivity and image resolution.

Carbon black represents a third example of the importance of the fumed materials to non-impact printing, as it is widely used both as pigment in black toners and ink jet inks.

2. Fumed inorganic materials in toner technology – materials with a wide array of properties

2.1 Fundamentals

The manufacturing process for fumed metal oxide materials typically consists of three fundamental steps: (1) core particle synthesis, (2) surface treatment, and (3) structure modification. The combination of these steps, which can be carried out continuously and/or batch-wise, allows the precise and tailor-made synthesis of external additives fulfilling the most stringent requirements of today's toner formulations.

Fumed silica and fumed metal oxides such as aluminum oxide (alumina) and titanium dioxide (titania) are manufactured by the hydrolysis of vaporized silicon and metal chlorides in an oxygen-hydrogen flame, for example, according the following equation [1]:

$$SiCl_4 + 2H_2 + O_2 \longrightarrow SiO_2 + 4\,HCl$$

The process results in aggregated, nano-structured metal oxides of high purity and low water content that have found diverse applications in industry.

During the manufacture of fumed silica and fumed metal oxides the vaporized silicon or metal precursor reacts with water (formed by the burning of hydrogen and oxygen) to create the individual silica or metal oxide particles. The conditions in the flame are such that the created particles, even within fractions of seconds, undergo many mutual collisions and thereby bond and sinter. This results in branched chain-like aggregates with a length of approx. 100 to 300 nanometers (Figure 1). The aggregates are the smallest actual units of the fumed metal oxides. Once the aggregates cool below the fusion point, additional collisions result in mechanical entanglement and hydrogen bonding of the chains. To distinguish this more friable state from aggregation this level of structure is described as agglomeration. In contrast to the sub-micron size of the aggregates the agglomerate particles may be from one to several hundred microns. Since agglomerates are only bound through weak forces, they can easily be broken down to aggregates during the blending process with toner, so that the latter are the dominant particle species in toner formulations.

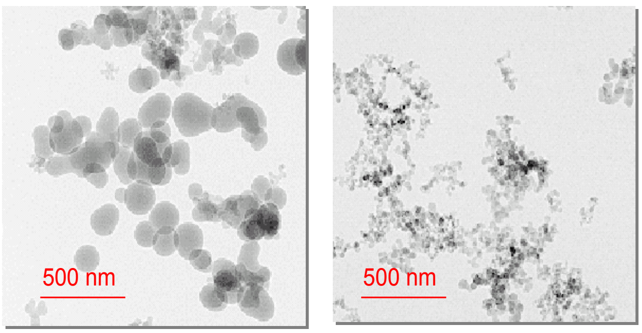


Figure 1: *Transmission Electron Microscopic images of medium (left) and small (right) primary particle size fumed silica*

The fumed silica process does also allow the manufacture of various mixed oxides such as the recently introduced silicon/titanium mixed oxides. Their structures largely depend on the ratio between TiO_2 and SiO_2. Materials with 5% silica content, for example, consist of a titania core and a silica shell (Figure 2).

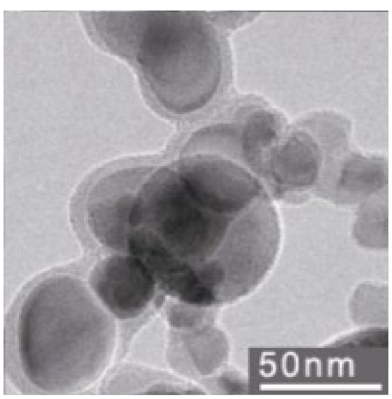


Figure 2: *Transmission Electron Microscopic image of a fumed silicon-titanium mixed oxide with a silica shell and a titania core.*

The primary particle size and the resulting aggregate size have a significant effect on the performance of a toner formulation. While products with a small to medium primary particle size of between 7 and 20 nm (medium to high specific surface area) are excellent free flow and tribo-charging agents, external additives consisting of primary particles between 30 and 100 nm are effective spacers which stay on the toner surface (that is, there is no embedding of external additive into the toner particle itself) and greatly improve durability.

The tribo-charging properties of an external additive are first and foremost determined by the electrical resistance of the base metal oxide itself (Table 1). Consequently, the tribo-charge of those products becomes increasingly more negative in the following order: fumed alumina < fumed titania < fumed silicon/titanium mixed oxides << fumed silica.

Table 1: Physical properties of silica, alumina, and titania

	Unit	SiO_2	TiO_2	Al_2O_3
Specific Gravity	$g\ cm^{-3}$	2.2	3.8	3.3
Refractive Index	-	1.46	2.5	1.7
Mohs Hardness	-	7	6	8
Electrical Resistance	Ωcm	1014	106	ca. 105
Melting Point	ºC	1610	1825	2015
Thermal Conductivity (300 K)	$W\ m^{-1}\ K^{-1}$	1.38	8.4	36

Another important inorganic material used in digital printing produced by a flame process is carbon black (Figure 3). Carbon black pigments are manufactured by the partial combustion of hydrocarbons according the following general reaction equation:

$$C_nH_{2n+1} + (2n+1)/4\ O_2 \longrightarrow nC + (n+1/2)\ HO_2$$

Properties of carbon black pigments, such as primary particle size and aggregate structure, can be controlled in a wide range by the process conditions similar to fumed silica and fumed metal oxides [2].

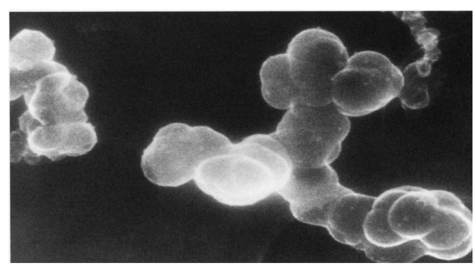


Figure 3: *Scanning Electron Microscopic image of carbon black aggregate (120,000 magnification)*

As seen in the SEM micrograph, carbon black is very similar in structure to fumed metal oxides. In both cases primary particles 10 – 80 nm build up to larger aggregates of several 100 nm in size. Carbon black has been the basic pigment in ink for millennia and continues its essential role today for the non-impact printing revolution. Besides the fundamental advantages from superior jetness, excellent tint strength, and environmental stability, carbon black is used in toner as an important ingredient in the overall design of electric properties.

2.2 Safety Issues

Fumed metal oxides and carbon black pigments are used in a wide range of applications. Therefore the toxicological profile of these materials is greatly important with respect to consumer safety as well as workers safety during the processing of the materials.

Fumed silica, alumina, titanium dioxide, and carbon black are regarded as safe from the view points of acute toxicity, skin irritation, skin sensitization, mutagenity and reproductive toxicity. Also, repeated dose exposure to skin and oral intake did not give any critical result. With respect to carcinogenity, fumed silica is classified by IARC with a 3 rating, which means it is not regulated. On the other hand carbon black and titanium dioxide are classified with a 2B rating which means both materials are regarded possible human carcinogens.

Long term investigations on large groups of workers at carbon black facilities in Germany (Kalscheuren), the UK and the USA were carried out on behalf of the International Carbon Black Association. The results from these mortality studies show no link between exposure to carbon black and higher lung cancer mortality rates in humans.

As for the long term exposure to fumed titanium dioxide, regular medical check-ups were carried out at the Evonik titanium dioxide manufacturing facility in Germany (Rheinfelden) over a number of years and no evidence of a higher incidence of respiratory disease compared with the general population was found. These findings were confirmed by subsequent epidemiological studies by other European and US titanium dioxide producers. These producers, together with Evonik, examined the impact of inhaled titanium dioxide dust in studies where rats, mice, and hamsters were exposed to air containing different concentrations of titanium dioxide dust for up to 90 days. Importantly, all three species exhibited changes to lung tissue only after exposures to extremely high doses (250 mg/m^3). At a lower concentration of 0.5 mg/m^3, which corresponds to the level found at the Evonik manufacturing facility, no tissue damage was found. At 2 mg/m^3, which is the workplace exposure limit in Germany, slight changes in tissue where observed only in rats.[3,4,5]

3. Fumed inorganic materials in toner technology — more than just a free flow agent

3.1 Basic functions of fumed inorganic particles

Fumed metal oxides have been used as external additives in toner for about 30 years. At the beginning, dimethyldichlorosilane treated fumed silica was the most widely used additive. This material has a moderate degree of hydrophobicity and imparts good free flow to toners at low addition rates like 0.1–0.3 %. With such additives, the toner charge is controlled mainly by addition of charge controlling agents (CCA).

The carbon blacks used at first for non-impact printing were the same grades as used in traditional printing ink applications. Now grades are available specifically tuned to the technical demands of either toner or ink jet applications. Beside the basic function as color pigment, carbon black, since it is a conductive material, also functioned as counterbalance to the nonconductive silica during electrification of the toner particles.

In recent years, raw material requirements for toners going into printer and copying machines have diversified due to a variety of system developments such as multi-purpose use, the trend to smaller machines, energy-saving, and new application areas like digital presses for high volume printing. Due to this increase in system complexity, more accurate material design is needed in the development of very fine particle toners, chemically produced toners, and color toners. As a result, modern toners use combinations of several external additives in a total concentration of up to 5%.

The complex role of external additives used for toners are depicted in Table 2 [6,7,8].

Table 2: Required properties in design with external additives at each stage of the printing process

Process Step	Additive Design Factor
Storage	Environmental Stability Anti-caking Charge Stability
Feed	Flowability Admixing
Mixing	Electrification Speed Dispersability Admixing
Development	Electrification Separation from Carrier Admixing Environmental Stability
Transfer/Separation	Electrification Adhesiveness De-agglomeration
Cleaning	Particle Size De-agglomeration Flowability Adhesiveness

3.2 Technical trends in toner development versus requirements towards inorganic fumed materials development

To optimize selection of an external additive for toner several factors need to be considered: type of toner (monochrome or color; milled or chemically produced), the type of machine (analogue or digital), and the type of photo-conductor (PC) drum (amorphous-silicon: a-Si or Organic Photo-Conductor: OPC). The numerous functions of external additives in the photo-electrographic process are summarized in table 3.

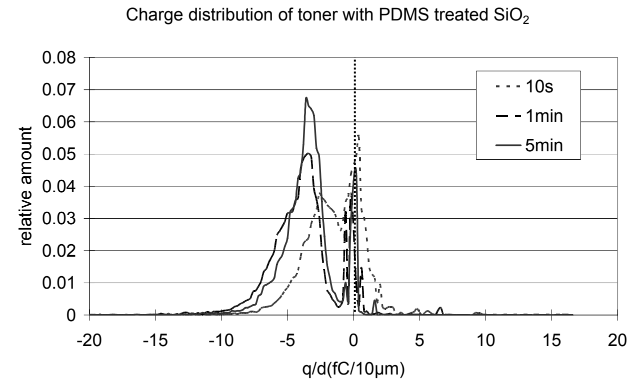
An appropriate external additive is selected by considering its physico-chemical properties (particle size and distribution, type of metal oxide and surface treatment) and then confirming the selection through complete applications tests. With the advancing requirements of electro-photography such as better image quality and higher process speeds, the need for more diverse as well as more durable external additives has made their selection process by the formulator more complex and critical.

Table 3: Trends in electro-photography and their impact on the use of inorganic fumed materials

Commercial and technical trends	Impact from fumed inorganic materials
Monochrome towards color toner	• Titania, silicon/titanium mixed oxides as low resistivity material
Milled toner towards chemically produced toner	• Higher diversity in additives due to larger variety in toner particle morphology • De-agglomerated additives for more "gentle" incorporation • Large primary particle silica and / or titania as spacer to improve durability • Easily dispersible carbon blacks easier to facilitate processing
Organic PC versus amorphous silicon PC	• More abrasive external additives like alumina facilitate drum cleaning
Electro-photographic color printing presses	• Tailored external additive combinations • Large primary particle silica and / or titania as spacer to improve durability • Titanium dioxide, silicon / titanium mixed oxides as low resistivity material
Low cost color printers	• Sometimes combination of lower cost external additives – even hydrophilic silica
Toner resins with lower fusing temperatures (T_g)	• Large primary particle silica and / or titania as spacer to improve durability.
Smaller toner particles	• Tailored external additive combinations • De-agglomerated additives for more "gentle" incorporation.

3.2.1 De-agglomerated external additives.

De-agglomerated external additives can be prepared by processes that break down the agglomerates of fumed metal oxides. In general, de-agglomerated additives can be dispersed with considerably less shear energy on the toner surface. The resulting distribution of aggregated particles on the toner surface is then more homogeneous and allows for faster "charge-up", a critical requirement for all new generation printers. As illustrated in figure 4, the rate of convergence, in other words, the charge-up of toner with de-agglomerated fumed silica is much faster compared to a toner with regular fumed silica. This phenomenon can be explained as follows: Agglomerated particles, although held to together by weak van-der-Waals forces, are much larger than toner particles. During external additive blending, these agglomerates need to be broken down before the resulting aggregates can be dispersed onto the toner surface. This de-agglomeration step is greatly facilitated when using de-agglomerated additives. De-agglomerated external additives are especially efficient for toner made from low T_g resins which require gentle mixing with lower shear forces in order to not affect the toner morphology.



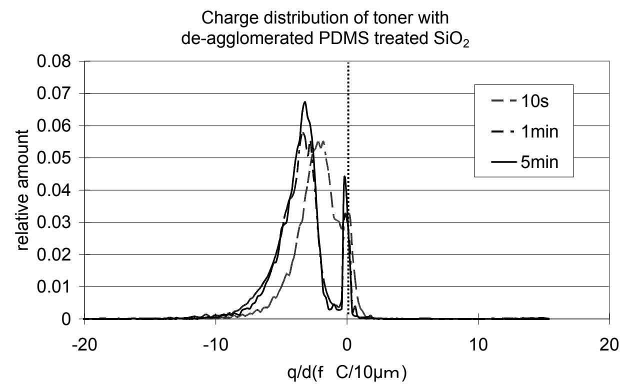


Figure 4: *Frictional electrification time of a toner with a regular silica additive (lower picture) in comparison to a de-agglomerated silica additive (upper picture).*

3.2.2 Large particle external additives.

Recent developments in toner technology have been made possible by the availability of large external additive particles. Large in this case means primary particles of silica or titanium dioxide with sizes ranging from 80 to 300 nm (such particles are often called sub-micron) – also, they are typically surface modified with hydrophobic agents. Lower T_g toner resins in combination with long agitation times, as occur in commercial printing presses, raise the likelihood that external additives are embedded into the toner particles and thereby lower their performance sometimes to the complete breakdown of the printing process. To counteract this, large additives particles should be considered when designing the external additive composition. These sub-micron additives act as spacers between colliding toner particles and keep small and medium size additive particles well dispersed on the toner surface for optimal free flow and tribo-charging.

The route to sub-micron silica until now has employed wet-chemical techniques (the so called sol-gel process). The resulting particles have a spherical morphology (aspect ratio approaching one) and a narrow particle size distribution. These characteristics should make possible a homogeneous charge, however as sphericity increases so does the challenge of maintaining good adhesion. Such ideal sphericity would not be expected from similarly sized fumed particles. Also, the sol-gel produced particles typically have a higher water content than do flame process particles and as a consequence a lower tribo-charge. For these reasons, the introduction of sub-micron fumed silica offers new advantages for toner formulators to investigate. (Figure 5).

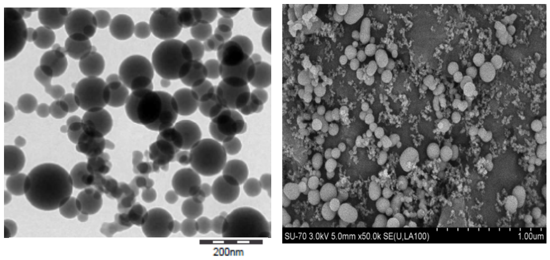


Figure 5: *TEM image of sub-micron fumed silica (left). SEM image (right) of toner surface with external additives combining small fumed silica particles with sub-micron fumed silica particles.*

3.2.3 Fumed silicon/titanium mixed oxides versus pure titanium dioxide.

Titanium dioxide is used in color toners to control the charge stability and charge distribution but it has the disadvantage that even surface treated with a highly hydrophobic silane the particle nevertheless does not exhibit strong hydrophobicity. This is in contrast to a similarly treated fumed silica particle. The reason for this difference is believed to originate in the relatively higher concentration of hydroxyl-groups on the titanium dioxide surface in comparison to silica. Adding a silica shell has been found to overcome this disadvantage and as a result silicon/titanium mixed oxides can provide a satisfactory charge distribution, excellent speed in electrification and even a better charge stability than pure titania (Table 4).[9,10] The properties of silicon/titanium mixed oxides can be further tailored by modification of the silica content and other structural parameters to match the requirements of each basic formulation.

Table 4: Comparison electrification behavior of silica, silica/titania mixed oxides and pure titania

	Fumed silica	Silica/titania Mixed oxides	Fumed titania
T-ESC	High	Medium	low
Charge Distribution	Wide	Middle	narrow
Charge-up Speed	Quick	Quick	slow
Charge Stability	Low	High	medium

3.2.4 Alternatives to Fumed Metal Oxides

Commercially relevant alternatives to fumed metal oxides as toner external additives are colloidal silica and certain wet process produced titanias. Colloidal silica particles have uniform spherical particle geometry and a quite uniform particle distribution. It has been speculated that such morphology could result in a more homogenous charge development for the toner particle but it is also expected to have some disadvantage with respect to adhesion of the particle on the toner surface.[11]

Wet process titanias make up a significant option in the external additive formulary. Special steps to avoid residual salts and water must be taken for these materials to perform properly; nevertheless they allow the toner designer the option of employing the electrification behavior of titania. From the example of wet process titania, recent investigations have begun into the use of similar forms of silica but obstacles remain due to the high porosity of such materials and the resulting difficulties at surface treatment with hydrophobic agents.

3.2.5 Developments for carbon black in Non-Impact Printing

Even though carbon black has been a basic pigment throughout civilization, modern techniques of production and modification have developed an array of grades that offer unique advantages to non-impact printing.

Dispersion, broadly described, is key to any effective pigment black. Dispersion within the toner resin or the ink vehicle for ink jet is fundamental to optimal performance. Over the years, methods to controllably oxidize the surface of carbon have resulted in a diversity of products for the formulator looking to achieve efficient pigment dispersion and stability. This surface chemistry design, along with other production process techniques, allows one to control the electrical resistivity for carbon black which is a key consideration to toner development.

Carbon black particle size and morphology play key roles in determining the jetness and tint strength of the pigment as well as the hold-out of an ink jet ink on a paper surface. Ways to control these parameters have also greatly evolved during the past few decades.

Finally, due to the high concern for exposure to any possible carcinogen, both toner and ink jet manufacturers put particular value on using carbon black sources with known low levels of polyaromatic hydrocarbons (PAH's, suspect carcinogens).

4. Summary

Looking at fumed inorganic materials in electro-photography we can see a number of properties directly related to the inherent high purity and unique particle nature (including composition, and structure) achievable only through flame manufacturing processes. These processes, combined with advanced surface chemistry treatments, lead to a wide array of unique products for the evolving technical demands of the non-impact printing world.

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In 2008 Dr. Paul Brandl was named Vice President of Research & Applied Technology for Evonik Degussa Inorganic Materials Asia/Pacific. He directs global external additive development and regulatory support for external additives based on fumed metallic oxides in toners. As Director of R&D for Nippon Aerosil Company in Yokkaichi Japan from 2001 - 2008, he was in charge of the development of novel materials for the toner and ink jet paper industry like structure-modified silica, Silica/Titania mixed oxides and large particle silica. NIPPON AEROSIL is part of the Evonik Degussa GmbH family of companies. Dr. Brandl has been with Evonik Degussa for more then 15 years, involved in various aspects of R&D and Technical Service.